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Local air pollution and long–range mass transport of atmospheric particulate matter: A comparative study of the temporal evolution of the aerosol size fractions

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ABSTRACT

Long–range transport of polluted air masses can significantly affect surface particulate matter levels. PM_{10} and $PM_{2.5}$ daily–average ponderal values alone are not sufficient to investigate the occurrence of such phenomena and consequently do not give significant information for source apportionment. In this work, the analysis of aerosol size spectra and the study of the correlation of the fine and coarse modes of PM have been applied to individuate long–range transport episodes of polluted air masses. Dust–models and backward–trajectory analysis were supportive to local surface measurements of size distribution of PM in confirming the origins of remote sources of pollution. An application is discussed involving long range transport of desert dust over Italy that comparatively examined with a fine–PM pollution episode due to local sources.

During the study, the atmospheric stability/unstability conditions were followed through the trend of the natural radioactivity considered as tracer of the Planetary Boundary Layer.

Keywords:
Long-range transport
Aerosol size spectra
Coarse/fine mode correlation
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1. Introduction

Atmospheric particulate matter (PM) in the micrometer size range follows a bi–modal distribution, with a coarse mode including particles produced by mechanical processes, such as soil dust, cloud droplets and many biological particles (Seinfeld and Pandis, 1997) and a fine mode dominated by both primary anthropogenic pollution from combustion processes and gas–to–particle conversion (Friedlander, 2000; Almeida et al., 2005).

European standards for atmospheric PM, PM_{10} and $PM_{2.5}$, are set by the Directive 2008/50/EC (Directive EC, 2008). Annual average concentration of PM_{10} should not exceed 40 $\mu g\ m^{-3}$ with no more than 35 days of exceedance of the daily limit value of 50 $\mu g\ m^{-3}$. As with regard to $PM_{2.5}$, the Directive recognizes that no threshold has been identified below which such pollutant would not pose a risk. Then, it adopts an approach aiming at a general reduction of concentrations in the urban background defining a limit value and a target value. A national exposure reduction target up to 20% should be met by 2020, while concentrations below 20 $\mu g\ m^{-3}$ are to be achieved by 2015, based on a three–calendar year running annual average concentration. Throughout their territory Member States will have to comply with the $PM_{2.5}$ limit value of 25 $\mu g\ m^{-3}$, by 2015 or, possibly, already by 2010.

Surface levels of PM have been widely reported to be affected by the long range transport of polluted air masses. Southern European regions, in particular the Mediterranean basin, are frequently influenced by dust transported from North Africa (Sahara and Sahel deserts) (CAFE, 2004). This source is far less significant in the Northern latitudes owing to the greater distances and to the different meteorology of these areas.

On the contribution of natural sources, Directive 2008/50/EC states that exceedances of the limit values shall not be considered as such when they are a consequence of natural events, as long as Member States provide the necessary justifications for that.

To that purpose, PM_{10} and $PM_{2.5}$ daily–average ponderal values alone are not sufficient to give significant information on the source apportionment. More information can be obtained studying the size distribution of atmospheric PM and the temporal variation of the correlation between the coarse and fine modes. With this aim, such an approach has been applied in this study and two pollution episodes have been comparatively examined. The first episode occurred in March 2007 and linked to local sources while the second one in August 2007 was due to long–range dust transport.

2. Materials and Methods

The approach adopted relies on the analysis of the aerosol aerodynamic–diameter spectra to highlight the contribution of long–range transport of polluted air masses. To this purpose, the temporal evolution of the correlation of the coarse and fine fractions was studied. Dust–models and backward–trajectory analysis were supportive to local surface measurements of PM size distribution confirming the origins of remote sources of pollution.

The study was carried out in Montelibretti (42°06′0′′ N, 12°38′0′′ E; 48 m a.s.l.; main wind directions N–NE), a rural area in the Northern periphery of Rome (around 30 km far from Rome), where daily–average PM_{10} and $PM_{2.5}$ were measured and aerosol size–spectra were continuously taken. The site is representative of a location not directly influenced by anthropogenic activities.

2.1. Analysis of the aerosol aerodynamic diameter spectrum

Aerodynamic size distributions of atmospheric aerosols were measured by means of a TSI Aerodynamic Particle Sizer (model 3321, APS, Shoreview, MN, USA). The APS spectrometer measures the time of flight of single particles, when they are accelerated through a nozzle, using two overlapping laser beams (Dahneke and Flachsbart, 1972; Wilson and Liu, 1980). Particles are counted and sized, in the range from 0.5 to 20 µm (aerodynamic diameters), in 50 size channels. Size distributions were averaged on a 5–minute time–span. Particle mass concentrations have been calculated from number concentration by APS software, assuming 2 g cm^{-3} average particle density (TSI, 2000). Based on the positions of the two maxima shown by the aerosol size–spectra, the 0.58 µm and 3.52 µm APS size channels have been considered as representative of the coarse and of the fine fractions, to study the correlation between the two modes. At each hour of the day, with 5–minute time resolution, the Pearson's coefficient of correlation has been calculated, considering the data–points referring to the subsequent 24 hours. Such time–span has been considered since the phenomena investigated are on the time scale of several days.

The Quality Control (QC) and Quality Assurance (QA) system of the APS instrument is continuously performed by both analyzing the physical parameters (such as inlet pressure, sheath flow, air volume, total flow, voltage, laser power, laser current, sheath pump voltage, box temperature, photo diode temperature, photo diode voltage) regulating the entire analytical process (sampling and analysis) and evaluating the data quality (two procedures were followed: comparing data from two different APS instruments operated concurrently and participating to annual inter–comparisons with other laboratories equipped with such apparatus).

2.2. Evolution of the atmospheric boundary layer

Natural radioactivity as a tracer of Planetary Boundary Layer (PBL) dynamic (Pearson and Jones, 1965; Shweikani et al., 1995; Perrino et al., 2001) was assessed using a PBL Mixing Monitor (FAI Instruments). The instrument samples atmospheric PM on 47–mm membrane filters and measures the β–radioactivity of short–lived decay products of Radon by means of a Geiger detector.

2.3. PM_{10}, $PM_{2.5}$ and nitrate measurements

PM_{10} and $PM_{2.5}$ levels were measured by means of a SWAM 5a Dual Channel Monitor (FAI Instruments, Fontenuova, Italy). The instrument is an automatic sampling and mass measurement system, working with two independent sampling lines. The PM samples are accumulated on filtering membranes and their mass is determined by the β–attenuation technique.

Further, particulate nitrate in $PM_{2.5}$ samples have been measured by means of an Ambient Particulate Nitrate Monitor (model N8400, Rupprecht&Patashnick Co. Inc., East Greenbush, NY, USA). The instrument consists of a pulse generator, where sample conditioning, collection and flash vaporization on a NiCr strip takes place, and a NO_X Pulse Analyzer, where nitrogen oxides evolved from flash vaporization and nitrate reduction are quantified (Stolzenburg and Hering, 2000).

2.4. Models for support interpretation

The interpretation of the aerosol size spectra was supported by dust–models and backward–trajectory analysis to assess the origin of the long–range transported air masses (Lyamani et al., 2005; Sugimoto et al., 2005; Gogoi et al., 2008; Coz et al., 2009). Dust simulations were performed by the Navy Aerosol Analysis and Prediction System (NAAPS) predicting the distribution of tropospheric aerosols. The model, developed by the Naval Research Laboratory (NRL) in Monterey (CA, USA) (Naval Research Laboratory, 2010), is a modified form of the model developed by Christensen (Christensen, 1997). The NRL version uses global meteorological fields from the Navy Operational Global Atmospheric Prediction System (NOGAPS), analyses and forecasts on a 1×1 degree grid, at 6–hour intervals and 24 vertical levels reaching 100 mbar.

Backward–trajectories were calculated by means of the HYbrid Single–Particle Lagrangian Integrated Trajectory Model (HYSPLIT) (Draxler and Hess, 1997), available at the NOAA Air Resources Laboratory (ARL) (Air Resources Laboratory, 2010).

3. Results and Discussion

3.1. Local PM pollution episodes

The PM pollution episode observed in Montelibretti (Central Italy) in the period from March 10 to March 21, 2007 was also observed in Milan (Northern Italy) as shown respectively in Figures 1a and 1b, reporting PM_{10} and $PM_{2.5}$ data. The $PM_{2.5}$ trends passed from 12.3 µg m^{-3} (March 10) to 42.2 µg m^{-3} (March 17) and from 16.0 µg m^{-3} (March 10) to 64.1 µg m^{-3} (March 16), respectively in Montelibretti and in Milan, suggesting that the high PM_{10} values measured in the period investigated were mainly due to the contribution of the fine fraction.

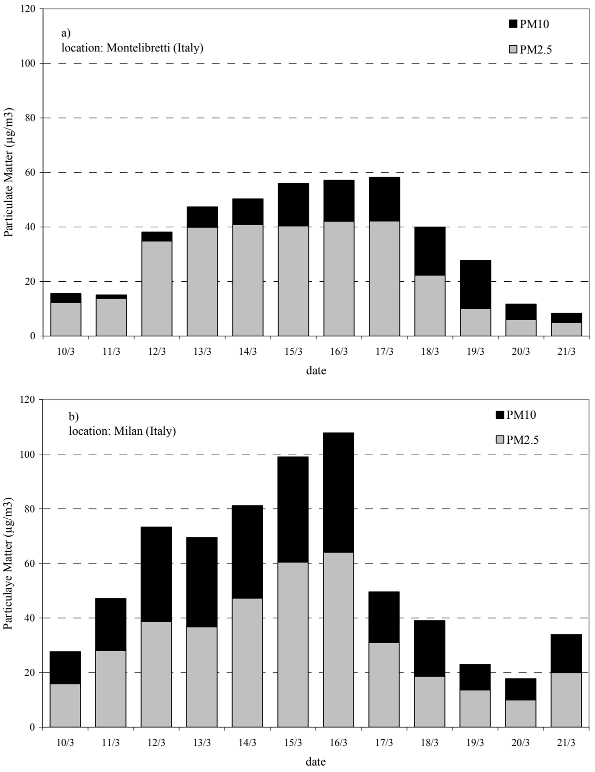

Figure 1. *Daily–average PM_{10}, $PM_{2.5}$ values measured in Montelibretti **(a)** and Milan **(b)** in the period of March 10–21.*

In line with the $PM_{2.5}$ trends, aerosol size spectra (Figure 2) in Montelibretti clearly shows a substantial increment of the fine fraction, that on March 17 at 08:00 reached values about 15 times higher than those measured on March 10 at 00:00.

The atmospheric pollution level is determined by both the intensity of its emissions and the dynamic properties of the atmospheric boundary layer, causing pollutant dilution or accumulation. In this respect, radon and its short–lived decay products can be considered as a tracer of the mixing properties of the lower boundary layer, since radon is emitted at a rate that is spatially and temporally constant, consequently, its concentration is mainly determined by the dilution properties of the atmospheric boundary layer (Pearson and Jones, 1965; Shweikani et al., 1995; Perrino et al., 2001).

The trend of variation of the fine fraction closely followed that of natural radioactivity as shown in Figures 3a and 3b, where the daily trends of the 0.58 (representative of the fine mode) and 4.06 µm APS size channel are reported together with the natural radioactivity.

Such occurrence suggests that the high levels of $PM_{2.5}$ were attributable to the presence of high pressure stable atmospheric conditions, presumable over a meso–scale area, given the same trend of PM_{10} and $PM_{2.5}$ observed in Montelibretti and Milan (Figures 1a and 1b), that favored the pollutant accumulation. On the contrary, the periods from March 10 to 11 and from March 19 to 21 were characterized by very low levels of natural radioactivity, very likely due to advective conditions that coherently favored pollutant dispersion, as shown by the low levels of the fine fraction (0.58 µm size channel in Figure 3a).

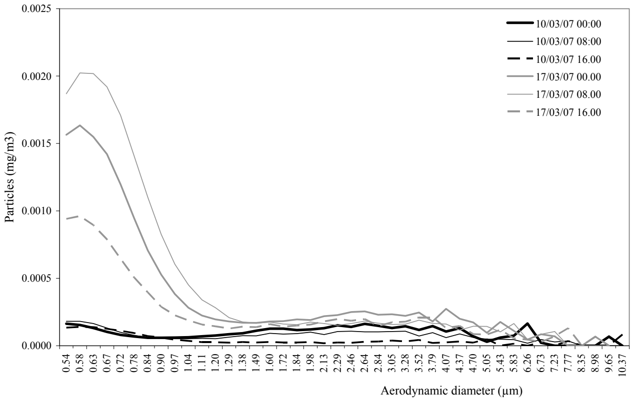

Figure 2. *Aerosol size spectra measured at different hours on March 10 and 17, 2007 in Montelibretti (Rome).*

Accordingly, the pattern of a secondary pollutant such as particulate nitrate (Figure 3c) followed very well that of the 0.58 µm APS size channel (correlation coefficient, R, 0.7), with an increasing trend when the atmospheric conditions favored the pollutant stagnation and the formation of secondary PM.

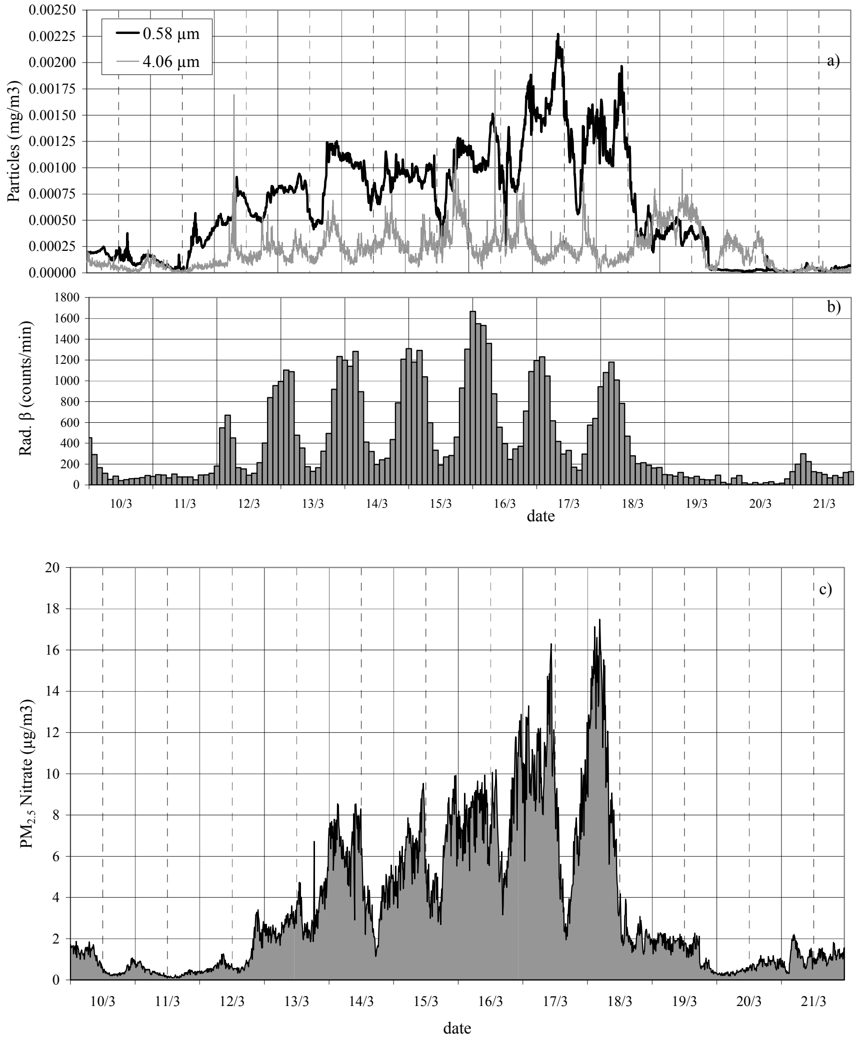

Figure 3. *Daily trends of the 0.58 and 4.06 µm APS size fractions* ***(a)****, and natural radioactivity in Montelibretti (Rome) in the period of March 10-21* ***(b)****, and daily trend of $PM_{2.5}$ nitrate concentration* ***(c)****.*

That the episode of March 2007 was due to local sources of pollution, amplified by stable atmospheric conditions, is further demonstrated by the very low wind velocity (average value below 1 m s^{-1}) measured during the period from March 13 to 18, in comparison with those measured during the periods of low natural radioactivity, from March 10 to 11 (average value above 3 m s^{-1}) and from March 19 to 21 (average value above 2 m s^{-1}).

3.2. Long–range PM transport episodes

In the period from August 20, 2007 to September 01, 2007, the trend of variation of PM_{10} in Montelibretti (Rome) was characterized by peak values of 54, 38 and 72 µg m^{-3} on August 22, 25, and 30, respectively (Figure 4).

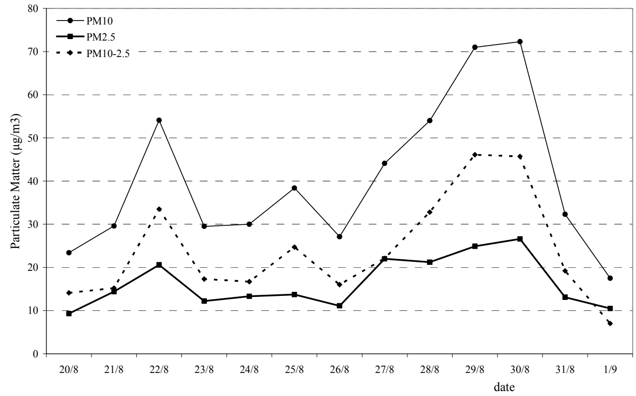

Figure 4. *Daily-average PM_{10}, $PM_{2.5}$ and $PM_{10\text{-}2.5}$ values measured in Montelibretti (Rome) in the period of August 20–September 01, 2007.*

When atmospheric pollution is dominated by local sources, PM_{10} daily average values as high as 40 µg m^{-3} are peculiarly expected on August in Rome. The PM_{10} levels measured in the period investigated, significantly higher than the expected values, were strongly suggestive of the occurrence of long–range air mass transport of PM. The same trend was followed by the coarse fraction ($PM_{10\text{-}2.5}$), evidencing that such fraction was responsible of the high PM_{10} values measured.

To investigate the scale of the pollution episode, PM_{10} values in Rome (ARPA Lazio) (ARPA Lazio, 2007) were compared with those measured in southern Italy in Brindisi (ARPA Puglia, 2007) and in northern Italy in Verona (ARPA Veneto, 2007) (Figure 5a). PM_{10} levels measured in Brindisi and in Rome shared the same trend of variation with three peak values, while in the PM_{10} pattern observed in Verona the first peak (on August 22) was lacking.

Figure 5b describes the APS aerosol size spectra measured in Montelibretti (Rome) at 00:00 on August 20 and September 02, before and after the PM_{10} events (Figure 4) and on August 23, 26 and 31, on the three PM_{10} peaks (Figure 4). Figure 5b shows significant increments of the coarse fraction, that, on August 23, 26 and 31, were respectively ~2.5, 1.5 and 3.5 times higher than the values measured on August 20.

As shown by aerosol size spectra measured in conditions of pollution dominated by local sources (Figure 2) and when also the contribution of remote sources is present (Figure 5b), particles in the $PM_{2.5}$ size range derive both from the fine and the coarse mode of PM, reflecting their double origin: anthropogenic and natural, not only in the case of long-range transport of polluted air masses. In particular, the advection of air masses transporting desert dust heavily affects PM_{10} as well as $PM_{2.5}$ levels (Figure 5b).

Figure 6a shows the daily trend of 0.54, 0.58, 0.63 µm, (representative of the fine mode) and of 3.52, 3.79, and 4.07 µm (representative of the coarse mode) APS size channels together with the Pearson's coefficient of correlation of 0.58 µm and 3.52 µm APS size channels (Figure 6b). The coarse and fine fractions vary from being well correlated to totally lacking of correlation. Moreover, in some periods the correlation coefficient has negative values indicating that one fraction varies along a decreasing trend, while the other follows an increasing pattern of variation. Such behavior can be understood observing the pattern of variation of the natural radioactivity (Figure 6d): when the radioactivity dropped, denoting higher degree of dilution of atmospheric pollutants, the fine fraction of PM (represented through the 0.54, 0.58 and 0.63 µm APS size channels) accordingly decreased, while, on the contrary, the coarse fraction (3.52, 3.79 and 4.07 µm APS size channels) increased (Figure 6c).

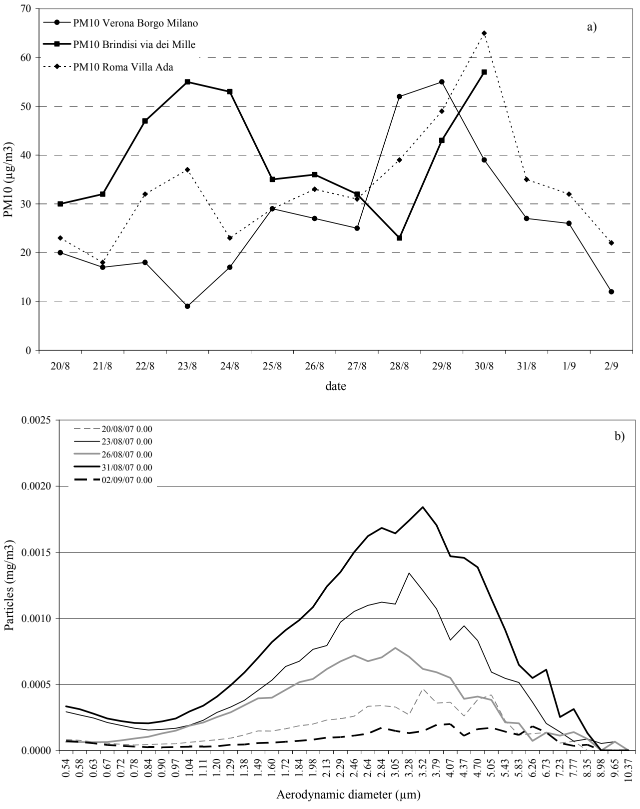

Figure 5. (a) *Daily–average PM_{10} values measured at ARPA monitoring stations in Brindisi, Rome, and Verona in the period of August 20–September 02, 2007;* ***(b)*** *Aerosol size spectra measured at 00:00 on August 20, 23, 26, and 31 and September 02, 2007 in Montelibretti (Rome).*

Such apparent contradiction (i.e. the degree of dilution of the low atmosphere increases and the coarse PM concentration increases too), is explained admitting a remote source of coarse PM, very likely transported through the inflow of new air masses.

When radioactivity dropped, due to the increased vertical degree of mixing, the coarse PM surface concentration increased, instead of decreasing, as a consequence of the mixing with the higher dust–rich atmospheric layers.

The origin of such dust is indicated by the NAAPS maps of dust surface concentrations (Figures 7a–7c) and by the HYSPLIT 96–hour backward trajectories to Brindisi (southern Italy), Rome (center–Italy) and Verona (north–Italy) at 1 500 m height (Figures 7d–7f) that, accordingly with the PM_{10} patterns recorded in these cities (Figure 5a), show no dust transport on August 21.

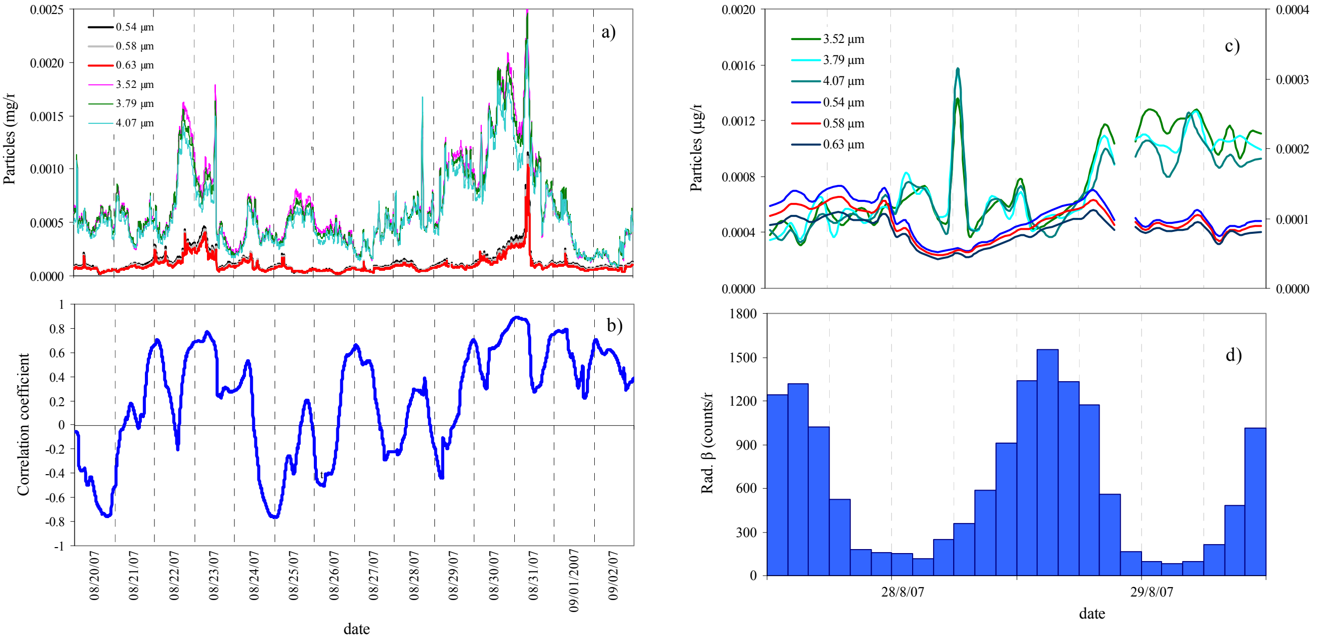

***Figure 6. (a)** Daily trends of the 0.54, 0.58, 0.63, 3.52, 3.79, and 4.07 µm APS size fractions in Montelibretti (Rome); **(b)** Pearson's coefficient of correlation of 0.58 µm and 3.52 µm APS size–fractions, from August 20 to September 02; **(c)** hourly averages of the 0.54, 0.58, 0.63, 3.52, 3.79, and 4.07 µm APS size fractions in Montelibretti (Rome) on August 28 and 29; **(d)** daily trend of natural radioactivity in Montelibretti in the period of August 28–September 29.*

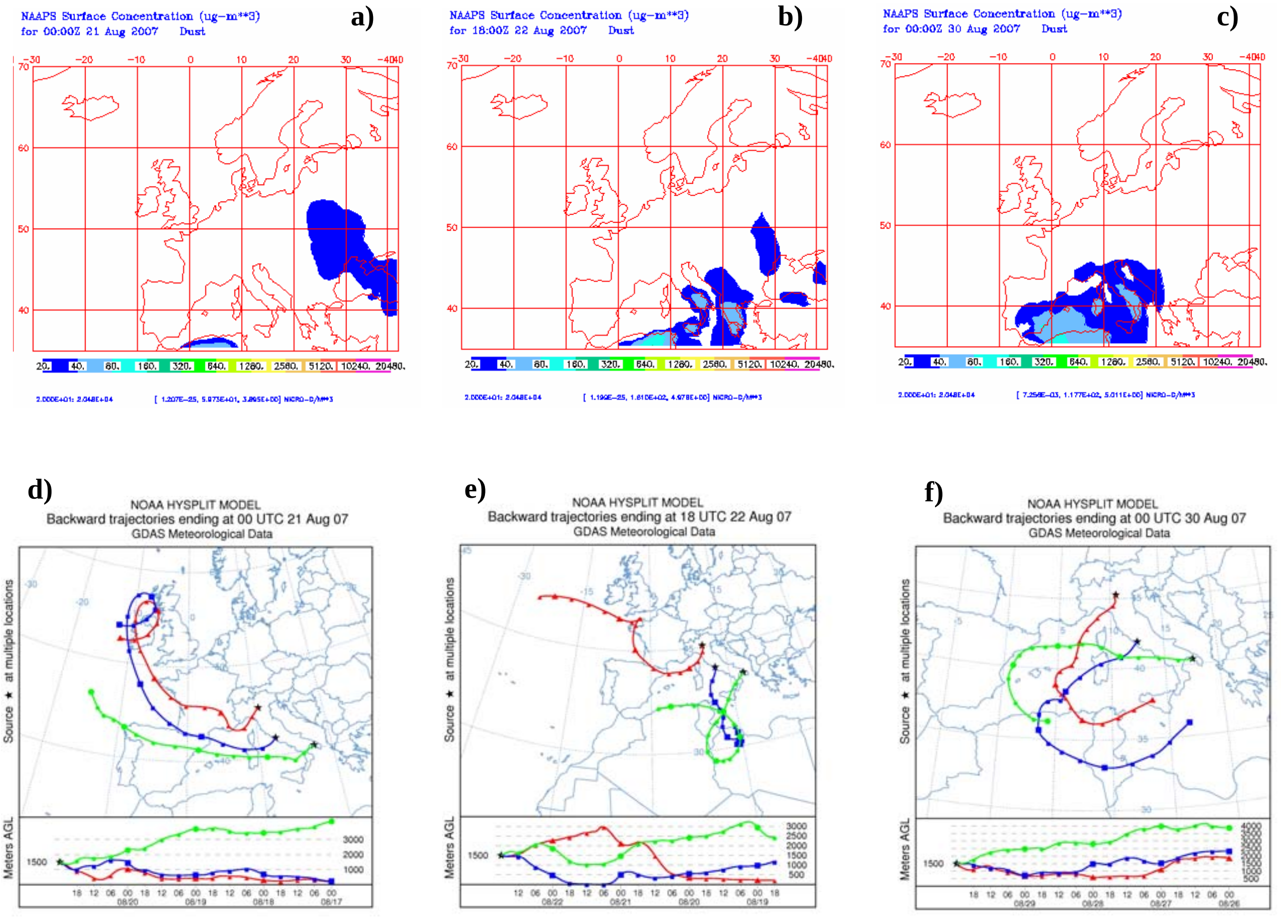

***Figure 7.** NAAPS "Dust" plots (above) at surface level on August 21 at 00 UTC **(a)**, August 22 at 18 UTC **(b)**, August 30 at 00 UTC **(c)**. HYSPLIT 96–h backward air mass trajectories (below) to Verona, Rome, Brindisi at 1500 m above ground level on August 21 at 00 UTC **(d)**, August 22 at 18 UTC **(e)**, August 30 at 00 UTC **(f)**.*

Advection of Saharan dust occurred on August 22, reaching Brindisi and Rome but not Verona, where, on that day, relatively low PM_{10} levels were measured (Figure 5a). On August 25 and 30 the inflow of desert dust involved the whole Italian peninsula (Figures 7c-7f).

4. Conclusions

Starting from the well–known issue that atmospheric stability and low wind velocities, as revealed by well structured and high levels of natural radioactivity, are conditions favoring pollutant stagnation and the formation of fine secondary PM, acute air pollution episodes determined by local sources can then be recognized in such situations, observing how the PM concentration pattern follows the behavior of natural radioactivity.

Dust from desert areas is transported at high altitudes and then produces high coarse PM surface concentrations in conditions of high vertical degree of atmospheric remixing, that otherwise would favor pollutant dilution. As a result of that, when natural radioactivity drops (high degree of remixing) the coarse mode concentration increases, while the fine fraction concentration decreases. The two modes then appear correlated negatively (negative values of Pearson's coefficient of correlation).

The results obtained draw the attention to the importance of highly time–resolved measurements in understanding the origin of atmospheric PM. The frequency of measurement should be comparable with the time scale of the evolution of the atmospheric PBL.

Moreover, aerosol size distributions have evidenced that the $PM_{2.5}$ convention includes particles both from fine and coarse modes. Therefore, the opportunity of adopting $PM_{2.5}$ as a descriptor of fine PM, should be matter of reflection (or, better, re–considered).

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